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catena-Poly[[[tetrakis(1-methylimidazole-κN^3)copper(II)]-μ^2-sulfato-$\kappa^2 O$:O'] acetonitrile hemisolvate sesquihydrate]

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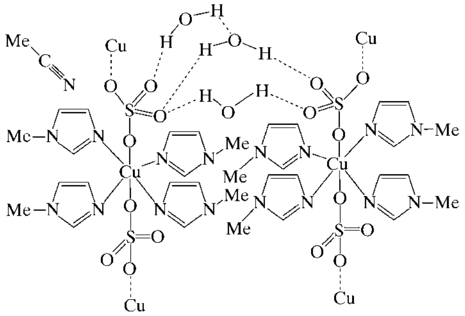
The title compound, $[Cu(C_4H_8N_2)_4]SO_4\cdot0.5CH_3CN\cdot1.5H_2O$, consists of a double chain wherein the Cu centres are octahedrally coordinated by four 1-methylimidazole ligands in the equatorial plane and by two axial sulfate ions which act as bridges between the Cu centres. The Cu—N bond lengths lie between 1.9929 (14) and 2.0226 (14) Å, but the Cu—O bond distances are longer, with values between 2.3496 (13) and 2.8276 (14) Å. The water molecules participate in the formation of a network of hydrogen bonds of significance in maintaining the connectivity of the structure.

Comment

Our research group is interested in the synthesis and characterization of thione complexes (García-Vázquez *et al.*, 1999). However, the pronounced tendency of S to bridge metal centres often produces insoluble polymers. In these cases, one strategy for the synthesis of low molecular weight compounds involves the incorporation of co-ligands to block some coordination sites. This technique has previously been successfully employed in the preparation of mixed thionate complexes (García-Vázquez *et al.*, 1999). As a continuation of this work, we attempted to synthesize a copper(I) complex incorporating a heterocyclic thionate and 1-methylimidazole as co-ligand. However, in the reaction of (1-propylimidazolidine-2-thionate)copper(I) with 1-methylimidazole, instead of the expected mixed-ligand copper(I) complex, the title compound, (I), was obtained. This compound is probably formed by oxidation of copper(I) and further replacement of the heterocyclic thionate ligand by 1-methylimidazole and sulfate ions, the latter formed by oxidation of the thionate sulfur in accordance with the process previously described by Raper (1994).

The coordination chemistry of tetrakis(imidazole)-copper(II) and its alkyl ligand derivatives has been widely studied and crystal structures have been obtained, mainly for the halides but also for oxoanions (Pan *et al.*, 1998, and references therein; Kohout *et al.*, 1999; Su *et al.*, 1995). Moreover, tetrakis(imidazole)copper(II) sulfate has been studied by X-ray diffraction (Fransson & Lundberg, 1972) and its structure shows a chain structure, but there are some differences from the compound described in the present paper (apart from the methyl group in the ligand). These differences are, in part, related to the supramolecular structure arising from the presence of water molecules, and to the absence of an inversion centre at Cu and the resulting lack of local symmetry (see below).



(I)

The structure of (I) is shown in Fig. 1 and selected bond distances and angles are given in Table 1. Compound (I) crystallizes as a linear polymer (Fig. 2). The asymmetric unit contains two formula units belonging to two different chains. The sulfate dianion acts as a bridge (μ-O:O') between the Cu centres. In addition, the other O atoms of the sulfate anions are involved in hydrogen-bond formation. Indeed, the framework is maintained by hydrogen bonds between the water molecules labelled O1 and O2 and sulfate anions of different chains, and water molecule O3 linking a sulfate ion and water molecule O2. Therefore, all H atoms in the water molecules are involved in hydrogen bonds. In the same way, all O atoms of the sulfate anions are involved in short interactions, either with Cu centres or water molecules, or through non-classical hydrogen bonds (Table 2).

The environment of both Cu atoms is octahedral, with the four 1-methylimidazole ligands in the equatorial plane and the O atoms of two symmetry-related sulfate ions in the axial positions. The bond lengths in the equatorial positions are similar to those found in the literature [see, for example, Su *et al.* (1995) or Potenza *et al.* (1988)] and do not merit further discussion. Each imidazole ring is planar to within ±0.003 (1) Å, while the methyl C atoms deviate by between 0.007 (3) and 0.069 (3) Å from these planes.

For the molecule labelled 1, the dihedral angles between each imidazole plane and the planar [±0.046 (1) Å] N_4-donor unit are 81.87 (6), 77.10 (6), 69.66 (5) and 78.80 (6)°, respec-

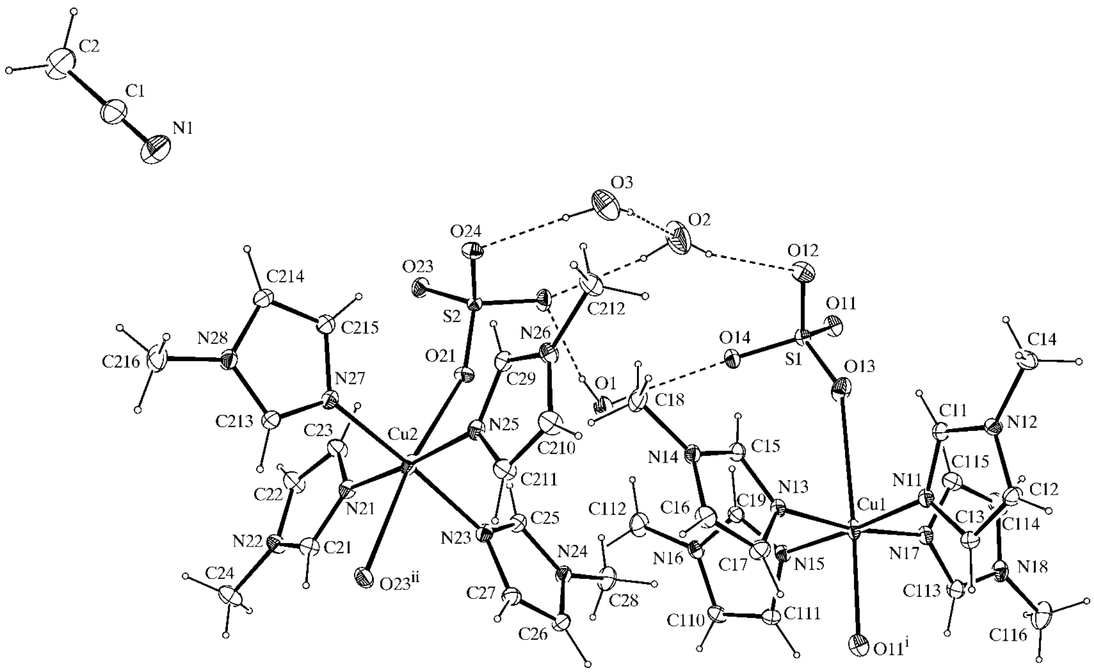


Figure 1

The asymmetric unit of (I) showing the atom-numbering scheme and the coordination sphere of the Cu atoms. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Symmetry codes are as in Table 2.

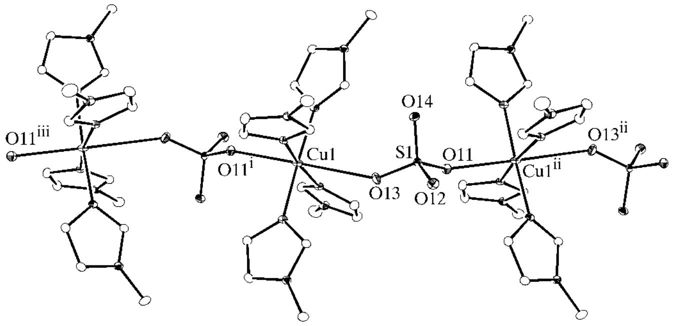


Figure 2

One of the chains of (I). For clarity, water and solvent molecules and H atoms have been omitted. [Symmetry codes: (i) as in Fig 1; (iv) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (v) $x, y - 1, z$.]

tively, and for the other four in molecule 2 with their planar [±0.071 (1) Å] N_4-donor unit, the dihedral angles are 77.75 (6), 67.12 (6), 66.27 (7) and 80.18 (6)°, respectively. The two N_4Cu units are slightly different; that centred on Cu1 has the metal 0.102 (1) Å out of the best plane defined by the four N-donor atoms, while this distance is only 0.013 (1) Å for Cu2. This deviation is due to the different coordination of the sulfate groups. Indeed, the Cu2—O distances have similar values, 2.5216 (13) and 2.6764 (13) Å, but the Cu1—O distances are 2.3496 (13) and 2.8276 (14) Å. This behaviour is not observed in the compound studied by Fransson & Lundberg (1972), where the value found is 2.574 (4) Å for both Cu—O distances, since the metal lies on a centre of inversion. These longer distances for the axial positions are well documented in the literature, mainly when the ligands in these positions are as poorly coordinating as sulfate.

Experimental

The title compound was prepared by reaction of an excess of 1-methylimidazole with (1-propylimidazolidine-2-thionate)copper(I), freshly prepared by an electrolytic method (Cabaleiro *et al.*, 2000), in refluxing acetonitrile for 3 h. After this time, a dark-blue precipitate was isolated and recrystallized from acetonitrile to give crystals of (I) suitable for structure analysis.

Table 1

Selected geometric parameters (Å, °).

Cu1—N11	2.0059 (14)	Cu2—N21	2.0012 (14)
Cu1—N13	2.0193 (14)	Cu2—N23	1.9951 (14)
Cu1—N15	1.9930 (14)	Cu2—N25	2.0225 (14)
Cu1—N17	2.0203 (14)	Cu2—N27	1.9950 (14)
Cu1—O11^{i}	2.3496 (13)	Cu2—O21	2.5216 (13)
Cu1—O13	2.8276 (14)	Cu2—O23^{ii}	2.6764 (13)
S1—O11	1.4748 (12)	S2—O21	1.4700 (12)
S1—O12	1.4833 (13)	S2—O22	1.4889 (13)
S1—O13	1.4714 (14)	S2—O23	1.4753 (13)
S1—O14	1.4796 (13)	S2—O24	1.4824 (12)
N11—Cu1—N13	88.44 (6)	N21—Cu2—N23	90.44 (6)
N11—Cu1—N15	176.48 (6)	N21—Cu2—N25	174.89 (6)
N11—Cu1—N17	90.74 (6)	N21—Cu2—N27	89.67 (6)
N11—Cu1—O11^{i}	91.62 (5)	N21—Cu2—O21	85.12 (5)
N11—Cu1—O13	85.30 (5)	N21—Cu2—O23^{ii}	96.28 (5)
N13—Cu1—N15	89.86 (6)	N23—Cu2—N25	91.43 (6)
N13—Cu1—O11^{i}	89.46 (5)	N23—Cu2—N27	176.65 (6)
N13—Cu1—O13	83.94 (5)	N23—Cu2—O21	86.70 (5)
N13—Cu1—N17	171.55 (6)	N23—Cu2—O23^{ii}	85.62 (5)
N15—Cu1—N17	90.49 (6)	N25—Cu2—N27	88.75 (6)
N15—Cu1—O11^{i}	91.45 (5)	N25—Cu2—O21	90.23 (5)
N15—Cu1—O13	91.46 (5)	N25—Cu2—O23^{ii}	88.61 (5)
N17—Cu1—O11^{i}	98.98 (5)	N27—Cu2—O21	96.64 (5)
N17—Cu1—O13	87.61 (5)	N27—Cu2—O23^{ii}	91.04 (5)
O11^{i}—Cu1—O13	172.78 (4)	O21—Cu2—O23^{ii}	172.20 (4)

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $-x, y - \frac{1}{2}, \frac{1}{2} - z$.

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Crystal data

$[Cu(C_4H_8N_2)_4]SO_4{\cdot}0.5C_2H_3N{\cdot}1.5H_2O$
$M_r = 535.58$
Monoclinic, $P2_1/c$
$a = 18.6227$ (1) Å
$b = 14.2708$ (1) Å
$c = 17.5255$ (1) Å
$\beta = 91.650$ (1)°
$V = 4655.66$ (5) Å^3
$Z = 8$
$D_x = 1.528$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 1.1$–28.3°
$\mu = 1.08$ mm^{-1}
$T = 293$ (2) K
Block, blue
0.20 × 0.16 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Siemens, 1996)
$T_{\min} = 0.809$, $T_{\max} = 0.881$
31 303 measured reflections
11 509 independent reflections
9721 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\max} = 28.3°$
$h = -24 \rightarrow 15$
$k = -18 \rightarrow 18$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.077$
$S = 1.05$
11 509 reflections
668 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0318P)^2 + 2.923P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.70$ e Å^{-3}

Aryl H atoms were placed in calculated positions and refined using a riding model, with C—H = 0.93 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. Methyl H atoms were located from ΔF syntheses and refined as part of a rigid rotating group, with C—H = 0.96 Å and $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$. Water H atoms were located in ΔF syntheses and refined freely.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1998); software used to prepare material for publication: *SHELXL*97.

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Table 2
Geometry of the classical and non-classical hydrogen bonds, and short contacts (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O22	0.81 (3)	1.97 (3)	2.780 (2)	171 (3)
O1—H1B···O14	0.73 (3)	2.08 (3)	2.806 (2)	173 (3)
O2—H2A···O14	0.79 (4)	2.84 (3)	3.486 (2)	141 (3)
O2—H2A···O12	0.79 (4)	2.10 (4)	2.869 (3)	164 (3)
O2—H2B···O22	0.81 (4)	2.09 (4)	2.866 (3)	159 (3)
O3—H3B···O2	0.73 (3)	2.17 (3)	2.888 (3)	168 (3)
O3—H3A···O24	0.83 (3)	1.97 (3)	2.793 (2)	177 (3)
O3—H3A···O22	0.83 (3)	2.95 (3)	3.496 (2)	125 (2)
C13—H13···O14$^{\rm i}$	0.93	2.48	3.327 (2)	152
C110—H110···O12$^{\rm iii}$	0.93	2.18	3.092 (2)	166
C111—H111···O12$^{\rm i}$	0.93	2.47	3.361 (2)	160
C113—H113···O12$^{\rm i}$	0.93	2.31	3.203 (2)	161
C212—H21A···O3	0.96	2.51	3.368 (3)	148
C29—H29···O24	0.93	2.44	3.353 (2)	167
C11—H11···O13	0.93	2.41	3.093 (2)	130
C19—H19···O14	0.93	2.20	3.125 (2)	173
C21—H21···O24$^{\rm ii}$	0.93	2.24	3.164 (2)	174
C213—H213···O22$^{\rm ii}$	0.93	2.35	3.252 (2)	164
C214—H214···N1	0.93	2.50	3.337 (3)	149

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $x, -\frac{1}{2} - y, z - \frac{1}{2}$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1479). Services for accessing these data are described at the back of the journal.

References

Cabaleiro, S., Castro, J., García-Vázquez, J. A., Romero, J. & Sousa, A. (2000). *Polyhedron*, **19**, 1607–1614.

Farrugia, L. J. (1998). *ORTEP-3 for Windows*. University of Glasgow, Scotland.

Fransson, G. & Lundberg, B. K. S. (1972). *Acta Chem. Scand.* **26**, 3969–3976.

García-Vázquez, J. A., Romero, J. & Sousa, A. (1999). *Coord. Chem. Rev.* **193–195**, 691–745.

Kohout, J., Hvastijova, M., Kozisek, J., García-Díaz, J., Valko, M., Jäger, L. & Svodoba, I. (1999). *Inorg. Chim. Acta*, **287**, 186–192.

Pan, L., Zheng, N., Zhou, X., Wu, Y., Wu, Q. & Jin, X. (1998). *Acta Cryst.* C**54**, 1802–1804.

Potenza, M. N., Potenza, J. A. & Schugar, H. J. (1988). *Acta Cryst.* C**44**, 1201–1204.

Raper, E. S. (1994). *Coord. Chem. Rev.* **129**, 91–156.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Siemens (1996). *SMART*, *SAINT* and *SADABS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Su, C.-C., Hwang, K.-Y., Chen, J. H., Wang, S.-L., Liao, F.-L. & Horng, J.-C. (1995). *Polyhedron*, **14**, 3011–3021.

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